Nuclear Solid State Physics using Ion Beams

Maria Fernanda da Silva

The research activity of the Nuclear Solid State Physics Group is focussed mainly on the processing and characterisation of advanced materials using ion beam based techniques.

The main output of the activity is the training of young researchers and students and is visible in the publications of the group.

The group, formed with staff from ITN and the Nuclear Physics Centre of the University of Lisbon, is responsible for the operation of the **Ion Beam Laboratory (IBL)** in Sacavém, with the 3.1 MeV van de Graaff accelerator and the 210 kV High fluence Ion Implantor and for **the two hyperfine interactions laboratories** located at the Nuclear Research Centre in Lisbon and in Geneve (ISOLDE/CERN), respectively.

There are collaborations with other researchers from several Portuguese universities.
Also, considerable collaboration exists with foreign research teams, namely from the universities of Seville, Madrid, Surrey, Bonn, Knoxville (USA), Budapest, amongst others. Most of these collaborations started through bilateral contracts and the participation in international projects.

In 2000, 39 papers were published in International Journals and 18 accepted for publication. These include **studies on insulators such as $LiNbO_3$ and Al_2O_3** started a few years ago, **synthesis of new compounds, like metastable alloys in Al and Ti**, and several **silicides** produced by implantation, studies on **doping of GaN by ion implantation** of shallow p-type dopants, and on the properties of **transition and noble metals implanted into SiO_2**.
An **artificial neural network algorithm** was developed that analyses RBS data instantaneously.

It is worth mentioning the potential of the ion beam techniques for studies of thin films and multilayers. Relevant work was done in the characterisation of **magnetic thin films for magnetic spin valves and tunnel junctions.**

The group participates in the **European Fusion Development** agreement technology work programme through several tasks, namely the study of SiC/SiC_7 ceramic composites, the development of Ceramic Breeder and of Beryllium Pebble Beds, and the qualification of high performance steel.

The group works also at **ISOLDE/CERN** with the e^--γ Perturbed Angular Correlations and the Emission Channeling techniques, applied to studies of High-Tc superconductors and of colossal magnetoresistive oxides with radioactive isotopes and of lattice site location of transition metals in semiconductors.

It will be a challenge for the group to organise a proposal to justify the natural upgrading of the Ion Beam Laboratory with the acquisition of a Tandem Accelerator.

The main results of the research developed during 2000 are summarised in the following pages.

Research Team

Researchers(*)

- Maria Fernanda da Silva (Principal Researcher) (**Group Leader**)
- Eduardo Alves (Aux. Researcher)
- Rui Coelho da Silva (Aux. Researcher)
- Luis Cerqueira Alves, Research Assistant (75%)[1]
- Andreas Kling, Portuguese Research Reactor (5%)
- José G. Marques, Portuguese Research Reactor (5%)
- Nuno Barradas, Portuguese Research Reactor (5%)

- José Carvalho Soares (Full Professor)[2]
- António A. Melo (Associate Professor) [3]
- Manuel Ribeiro da Silva (Aux. Prof.), IST

- Mark Breese, (Invited Scientist) (10%)
- João Guilherme Correia, PRAXIS Post Doctoral at CERN
- António Paúl, PRAXIS Post-Doctoral
- Peng Wei, PRAXIS Post-Doctoral
- Liu Chang, PRAXIS Post-Doctoral

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Students

- Ana Rita Ramos, **PhD** student
- Luís Prudêncio, **PhD** student
- Ana Pascoal, **MSc** student
- Carlos Pedro Marques, **MSc** student
- Márcia Vilarigues, **MSc** student
- Carlos Jesus, **MSc** student, until June 2000
- Elizabete Rita, **Last Year BSc** Student

Technical Personnel

- Jorge Rocha
- Filomena Baptista

(*) Also members of CFNUL.
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[2] On leave from University of Lisbon.
[3] Retired from University of Lisbon.

Publications

Journals:	39 and 18 in press
Proceedings:	7 in press
Conf. Communications:	29
Theses:	1

Funding

	$\times 10^3$ PTE
Research Projects: (a)	50 582
Services:	2094
TOTAL:	52 676

(a)

$\times 10^3$ PTE

- Metallic Silicides Formed by Ion Implantation (PRAXIS/2/2.1/FIS/438/94) (1997-2000) (36 000 $\times 10^3$ PTE $\rightarrow$ ITN/13000 $\times 10^3$ PTE) ITN/Co-ordinator**: M. Fernanda da Silva**, Partners: CFNUL (J. Carvalho Soares), INESC (P.P. Freitas) 5000
- Fusion Program (Sub-tasks: TW0-T431/01/TTMA-001/TTMS-006) 24 538 $\times 10^3$ PTE ITN/Co-ordinators: **Eduardo Alves** and **J. Carvalho Soares** 24 538
- e-γ Hiperfine Interactions at ISOLDE/CERN (CERN/P/FIS15180/99) (14 000 $\times 10^3$ PTE) ITN/Co-ordinator**: J. Carvalho Soares** 14 000
- Formation of Metallic Nanocrystals in Sapphire and Rutile by ion Implantation (PRAXIS/P/CTM/12067/98) – (1998-2001) (6000 $\times 10^3$ PTE) ITN/Co-ordinator**: Eduardo Alves**, Partners: FFCUL 1800
- Irradiation of Biomaterial Implants for Head and Neck Oncological Patients (PRAXIS/PSAU/C/120/96) (1998 – 2001) (15 000 $\times 10^3$ PTE $\rightarrow$ ITN/5000 $\times 10^3$ PTE) ITN/Co-ordinator**: Eduardo Alves**, Partners: IPO 3375
- Metastable Alloys in Al-Cr System, Produced by Ion Implantation and Laser Processing (PRAXIS/PCEX/P/FIS/2/96) (1997 - 2000 (14 700 $\times 10^3$ PTE) ITN/Co-ordinator**: Rui C. da Silva**, Partners: FFCUL (Olinda Conde) 1869
- Doping Effects on the Behaviour of Mixed Valence Oxides Ceramics with Strongly Correlated Electrons (PRAXIS/P/CTM/13142/98) (1998 – 2001) (20 000 $\times 10^3$ PTE $\rightarrow$ ITN/2200 $\times 10^3$ PTE)
- Contract Co-ordinator: Univ. Aveiro (J.M. Vieira), Partners: ITN (**Eduardo Alves**) —
- Metastable Alloys in Ti-Cr System, Produced by Ion Implantation and Laser Processing (PRAXIS/P/CTM/10037/98) - 1997 - 2000 (7500 $\times 10^3$ PTE $\rightarrow$ ITN/4380 $\times 10^3$ PTE) ITN/Co-ordinator**: Rui C. da Silva**, Partners: IST, FFCUL .... —

Ion Beam Analysis and Ion Beam Modification of Insulating Materials

A. Kling[1)], E. Alves, R.C. Silva, L.C. Alves, C. Jesus, C. Marques, A. Falcão[2)], M.F. da Silva, J.C. Soares, T. Monteiro[3)], J. Soares[3)], L. Santos[3)], O. Conde[4)] , J.A. Sanz-García[5)], J. García-Solé[5)], F. Agulló-López[5)], D. Bravo[5)], C. Zaldo[6)], J. Carvajal[7)], R. Solé[7)], F. Díaz[7)], I. Földvári[8)], Á. Péter[8)], K. Polgár[8)], E. Szilágy[9)], P.F.P. Fichtner[10)], L. Amaral[10)], F. Zawislak[10)], C. McHargue[11)], J.D. Hunn[11)], P.J. Sellin[12)], M.B.H. Breese[12)], A.P. Knights[13)], R.S. Sussmann[14)], A.J. Whitehead[14)]

Objectives

Extrinsic and intrinsic defects determine the physical properties of insulating materials to a large extent. Ion beams provide powerful tools to study these defects by means of Rutherford backscattering (RBS) and Particle Induced X-Ray emission (PIXE) under channeling conditions. In addition, the use of a microbeam facility enables to obtain information on the elemental distribution and electrical properties with high spatial resolution. On the other hand ion implantation can be used to engineer the defect structure of materials or to create new kinds of materials. The combination of these ion beam techniques with electron microscopy, optical and other methods provides deep inside into relevant properties of insulators.

Results

• Recent studies on the **lattice location of cationic dopants in lithium niobate** indicated that their incorporation depends on the valence state (for valence +1 to +4 they replace Li, for +5 and +6 Nb). It is known that uranium in melt-doped $LiNbO_3$ is present in the form of U^{6+} but can change its valence state to U^{3+} and U^{4+} during thermal reduction. RBS/channeling studies on the lattice site of U in as-grown crystals and samples reduced at 1000ºC for 16 hours in high vacuum show that about 20% of the uranium atoms located on Nb sites in the as-grown material are transferred to Li sites during the reduction treatment [1]. In addition, the lattice location of Co in melt-doped $LiNbO_3$ has been determined [2]. RBS/channeling measurements were further used in order to investigate the relationship between inpurity concentration and structural properties of growth domains in $KTiOPO_4$ on the one hand their optical properties on the other [3].

• **Implantation of He ions into $LiNbO_3$** is known to produce a buried damaged layer with a reduced refractive index which enables the formation of high quality optical waveguides in this material. Despite of the technological importance of this fabrication method, information about the type of defects introduced by ion implantation and subsequent low temperature annealing was not available so far. RBS/channeling studies revealed an increase of damage during heat treatment for temperatures up to 270ºC. First TEM micrographs of samples implanted with 10^{16} cm^{-2} He^+ ions of 20 keV energy and annealed at 270ºC for 4 hours revealed the existence of overpressurized He bubbles in this material [4].

• Another important modification of optical materials is the formation of **noble metal nanoclusters**. For the first time the formation of Au nanoclusters in bismuth tellurite (Bi_2TeO_5) was demonstrated using implantation of 800 keV Au^+ ions into single crystalline samples and subsequent annealing in two different annealing ambients. Measurements of the optical absorption in air-annealed samples enabled to estimate the average radii of the Au colloidal particles to be in the range of 3-4 nm [5]. The recrystallization of the host lattice seems to be hampered by the formation of these nano-particles although annealing in vacuum yields a considerable lattice recovery.

• Besides its relevance in several high technology areas **α-Al_2O_3** is also of increasing importance in the rapidly growing field of optoelectronics. In our research work we use the ion implantation technique to introduce different elements in order to alter the optical and structural properties of sapphire. The influence of the implantation parameters (fluence, energy, substrate temperature and orientation, etc) and annealing atmosphere on the evolution and final state of the implanted crystals were studied in detail. The relevant results were presented in international conferences and already published or accepted for publication in scientific journals [6-11].

• **Ion beam induced charge (IBIC)** techniques with a nuclear microprobe were used to study the charge transport distribution in polycrystalline diamond produced by chemical vapour deposition. IBIC images showed spatially resolved regions of high charge collection efficiency correlating individual crystallites with a typical width of 20µm, as observed by secondary electron microscopy [12]. In addition, the ion beam induced luminescence (IBIL) technique was used and a comparison between IBIC and IBIL images reveals that regions with high luminescence yield have a low charge collection efficiency. Further, regions that display neither high charge collection nor high luminescence yield were found which probably correspond to regions of small crystallites.

Published (or in press) work

[1] Kling, A., da Silva, M.F., Soares, J.C., Sanz-García, J.A., García-Solé, J., Change of Uranium Lattice Site in $LiNbO_3$ Induced by Thermal Reduction Treatment, *Radiation Effects and Defects in Solids*, accepted for publication.

[2] Szilágy, E., Becze-Deák, T., Bottyán, L., Kocsonya, A., Kótai, E., Nagy, D.L., Kling, A., Battistig, G., Khan, N.Q., Polgár, K., Lattice Site Determination of Co in Low Doped Congruent $LiNbO_3$ Single Crystal Using PIXE/Channeling, *Solid State Commun.* **115** (2000) 535.

[3] Zaldo, C., Carvajal, J., Solé, R., Díaz, F., Bravo, D., Kling, A., Influence of impurities on the optical damage of $KTiOPO_4$ crystals, *J. Appl. Phys.* **88** (2000) 3242.

[4] Kling, A., da Silva, M.F., Soares, J.C., Fichtner, P.F.P, Amaral, L., Zawislak, F., Defect Evolution and Characterization in He-Implanted $LiNbO_3$, *Nucl. Instr. Meth. B*, accepted for publication.

[5] Kling, A., da Silva, M.F., Soares, J.C., Fichtner, F.P.F., Amaral, L., Zawislak, F., Földvári, I., Péter, Á., Formation of Nanoclusters in Au-Implanted Bismuth Tellurite, *Nucl. Instr. Meth. B*, accepted for publication.

[6] Alves, E., da Silva, M.F., Soares, J.C., Monteiro, T., Soares, J., Santos, L., Effect of Crystal orientation on defect production and optical activation of Er implanted sapphire, *Nucl. Instr. Meth.* ***B*166-167** (2000) 183.

[7] McHargue, C., Hunn, J.D., Alves, E., da Silva, M.F., Soares, J.C., Influence of Oxygen Ion Implantation on the Damage and Annealing Kinetics of Iron-Implanted Sapphire, *Nucl. Instr. Meth.* ***B*166-167** (2000) 188.

[8] Alves, E., Silva, R.C., Jesus, C., Soares, J.C., da Silva, M.F., Conde, O., McHargue, C., *Surface Coatings & Technology* **128-129** (2000) 434.

[9] Marques, C., Cruz, M.M., da Silva, R.C., Alves, E., Study of new surface structures created on sapphire by Co ion implantation, *Nucl. Instr. Meth. B*, accepted for publication.

[10] Marques, C. da Silva, R.C., Falcão, A., Alves, E., Annealing behaviour of natural topaz implanted with W and Cr ions, *Nucl. Instr. Meth.* ***B*166-167** (2000) 204.

[11] Marques, C., Santos, L., Falcão, A.N., Silva, R.C., Alves, E., Luminescence studies in colour centres produced in natural topaz, *J. Luminescence* **87-89** (2000) 583.

[12] Sellin, P. J., Breese, M.B.H., Knights, A. P., Alves, L. C., Sussmann, R. S., Whitehead, A. J., Imaging of Charge Transport in Polycrystalline Diamond using Ion Beam Induced Charge Microscopy, *App. Phys. Lett.* **77** (2000) 913.

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Modification and Study of Semiconductors with Ion Beams

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Objectives

The continuously improving quality of epitaxial GaN films yielded a decrease of the background electron concentration to values of the order of 10^{16} cm^{-3}. This enables the doping of GaN using ion implantation of shallow p-type dopants which is one of the challenges in GaN research. The aim of the present research program is to study the ideal implantation conditions to dope GaN for the introduction of both electrical (Ca, Mn) and optical active ions (rare earths). Besides the main field of research on GaN studies on the properties of transition and noble metals implanted into silicon have been also performed.
A further line of studies concerns the technologically important technique of 'Smart-Cut®' for the slicing of Si wafers.

Results

In **GaN:Er** and **GaN:Er,O** samples implanted at RT and high temperature the sharpest zero phonon lines (FWHM ~0.4 meV) for Er-related infrared PL centres were detected using below band gap excitation. The characteristic multiline spectra and their dependence on the fluence and excitation energy indicate clearly that different Er-related optical centres, located in lattice sites with different symmetries, are responsible for the emission. For the first time well resolved green, red and infrared luminescence spectra from Er related centres were observed in Er and Er,O implanted MOCVD grown GaN samples. RBS measurements as well as the presence of GaN Raman lines and the PL spectra obtained by above band gap excitation in the visible region show that recrystallization of GaN can be achieved by annealing at high temperature under high nitrogen pressure. The annealing at 1200°C allows the complete epitaxial regrowth of the amorphized layer and the incorporation of a fraction of Er into well-defined GaN lattice sites. Fig. 1 shows the green region of the emission spectra and the corresponding level scheme for Er^{3+} incorporated into GaN by ion implantation [1,2].

The diffusion behaviour of Ir at a concentration below the threshold for the formation of **$IrSi_3$** was studied in the temperature range from 700 to 1000ºC. Iridium was introduced by ion implantation (energy: 130 keV, dose: 3×10^{16} cm^{-2}) into amorphous Si samples. Ir depth profiles were obtained by Rutherford backscattering measurements of various as-implanted and annealed samples (see Fig.2 for examples of Ir-related signal in the RBS spectra). The diffusion coefficient and the activation energy were found to be $D=2.61\times10^{-14}$ cm^2s^{-1} and $E_a=3.3$ eV, respectively [3].

Microprobe techniques are being used to investigate the behaviour of hydrogen bubble coalescence and induced material exfoliation in hydrogen-implanted 'Smart-Cut®' silicon. So far, it was shown that the crystal quality is altered far beyond the expected implantation-induced damage range supporting the production of a mechanically induced lattice deformation that was never observed before [4].

The influence of the crystallographic directions on the stopping power was studied along the <111> axis of a silicon single crystal. The measurements were performed with the three hydrogen masses [5].

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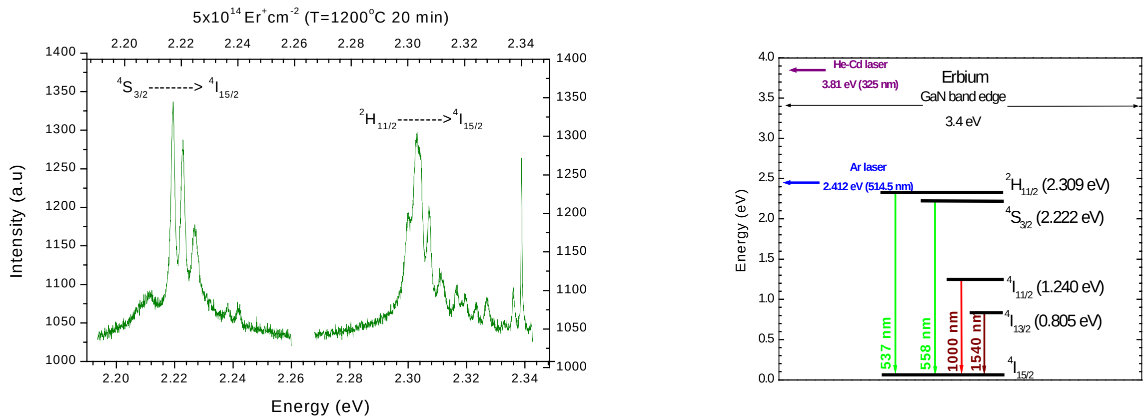

Fig. 1 - Green emission of Er doped GaN by Ion Implantation.

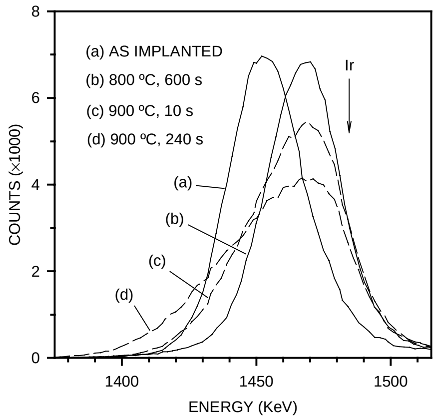

Fig. 2 - Ir-related RBS signal of samples annealed at different conditions.

Published (or in press) work

[1] Lorenz, K., Vianden, R., da Silva, M.F., Soares, J.C., Alves, E., RBS/Channeling study of Er doped GaN films grown by MBE on (111) Si substrates, *Nucl. Inst. and Meth.* **B161/163** (2000) 946.

[2] Alves, E., Monteiro, Y., Soares, J., Santos, L., sa Silva, M.F., Soares, J.C., Lojkowski, W., Kolesnikov, D., Vianden, R., Correia, J.G., High Temperature Annealing of Er implanted GaN, *Mat. Sci. and Engineering B*, in press.

[3] Rodriguez, A., González, C., Rodriguez, T., Kling, A., da Silva, M.F., Soares, J.C., RBS Characterization of the Iridium Diffusion in Silicon, *Nucl. Instr. and Meth.* **B161/163** (2000) 663-667.

[4] Breese, M.B.H., Alves, L.C., Hoechbauer, T., Nastasi, M., A Study of the Crystalline Quality of Exfoliated Surfaces in Hydrogen-Implanted Silicon, accepted for publication in *Appl. Phys. Lett.*

[5] Behar, M., Alves, E, Azevedo, G.M., Grande, P.L., da Silva, M.F., Soares, J.C., Molecular H_2 and H_3 Stopping Power Measurements Along ⟨100⟩ Si Channeling Direction, *Nucl. Inst. and Meth.* **B161/163** (2000) 168.

Artificial Neural Networks for Ion Beam Analysis

N.P. Barradas, A. Vieira[a], R. Patrício[b], E. Alves, C. Jeynes[c]

Objectives

Ion Beam Analysis (IBA) comprises several related techniques dedicated to the compositional analysis of samples, Rutherford backscattering (RBS) being one of the most widely used. Manual analyis of RBS is a time-consuming procedure that precludes the analysis of large amounts of data. It would be highly desirable to have push-button near-instantaneous data analysis, particularly for specific systems of interest. Furthermore, the experimental conditions must be optimised for each sample measured, and it would also be desirable to have a code capable of doing that automatically. The aim of this work is to develop a code based on a supervised feedforward Artificial Neural Network (ANN) that reaches these aims.

Results

An ANN algorithm was developed that analyzes RBS data instantaneously. It is a push-button black box, which opens the doors to the integration of RBS in the production line. The algorithm can be applied to a single system, albeit in a very wide range of implanted dose and depth, and of experimental conditions. For each different system to be studied, a new ANN must be built and trained. While this is clearly a shortcoming, many applications require the analysis of a large amount of similar samples, for instance, in quality control, or in batch production of given systems. We have already developed ANNs to several different cases, such as implants of Ge in Si, of Er in sapphire, and thin films of TaNiC [1-4].

We studied the error performance of the ANNs. We found that the behaviour of the ANNs depends critically on the data used in the training process. In particular, we showed that there is a trade-off between the generality of the ANN and its accuracy. We showed that ANNs designed for specific experimental conditions out-performs an ANN able to analyse data measured in any experimental conditions. We also concluded that the ANN error can be minimised by narrowing its field of applicability further, if previous knowledge over the implant parameters is available [5].

The ANNs developed were applied to real experimental data with excellent results. The error on the implanted dose was within the experimental error given by the limited counting statistics, and the error on the implanted depth was within the depth resolution of the technique. This means that the results given by the ANN can be taken directly as such, or used as the initial guess in a fast local optimization algorithm.

Published (or in press) work

[1] Vieira, A., Barradas, N.P., Neural network analysis of Rutherford backscattering data; *Nucl. Instrum. Methods* ***B*170** (2000) 235-238.

[2] Barradas, N.P., Vieira, A., Artificial neural network algorithm for analysis of Rutherford backscattering data; *Phys. Rev.* ***E*62** (2000) 5818-5829.

[3] Barradas, N.P., Vieira, A., Alves, E., Artificial Neural Network analysis of RBS data of Er-implanted sapphire; accepted by *Nucl. Instrum. Methods B.*

[4] Vieira, A., Barradas, N.P., Composition of NiTaC films on Si using neural networks analysis of elastic backscattering data; accepted by *Nucl. Instrum. Methods B.*

[5] Vieira, A., Barradas, N.P., Jeynes, C., Error performance analysis of Artificial Neural Networks applied to Rutherford backscattering data; accepted by *Surf. Interface Analysis*.

Further work

We will apply ANNs to more systems, as well as to other experimental techniques such as ERDA and NRA. We will work on developing code that is more general, for instance an ANN able to analyse data of implantation of any element into any lighter substrate eventually composed of more than one element. We will also develop code for automated control of the optimum experimental conditions for a given system in RBS analysis.

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Magnetic Spin Valves and Tunnel Junctions

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Objectives

Spin dependent tunnel junctions are of technological interest for applications in magnetic non-volatile random access memories due to their large tunnelling magnetoresistance effect and low junction resistance-area product. Magnetic spin valves are used in sensors as reading/recording heads for magnetic hard disk drives. These systems are undergoing extremely fast development as technical requirements become more stringent and their structure becomes more complicated. Typical structures can have 10 to 20 layers with thickness between 10 and 100 Å each. This poses an extreme challenge to the analysis of the layer structure in these systems, which is extremely important as it often determines the magnetic properties. The purpose of this work is to perform optimised ion beam analysis in order to understand and improve these complex systems.

Results

Spin valves with typical structures are Si/Al_2O_3 600Å/Ta 70Å/NiFe 70Å/CoFe 30Å/$Al_xN_yO_z$ t/CoFe 40Å/MnIr 200Å/Ta 30Å, with t=6-30 Å, annealed to temperatures up to 500ºC, were analysed [1-2,4-6]. Figure 1 shows a simultaneous fit obtained for heavy ion RBS, ERDA and He RBS data for one given sample.

From these data, the annealing process, which is fundamental in these structures since they must be annealed at temperatures around 400 ºC for fabrication of integrated circuits, was understood. Basically, the Al_2O_3 barrier layer remains essentially unchanged on annealing, while there is diffusion between the CoFe and MnIr layers. On the contrary, the signals corresponding to the NiFe layer and to the MnIr/Ta and Al_2O_3/CoFe interfaces remain approximately the same on annealing. This explains the changes in the

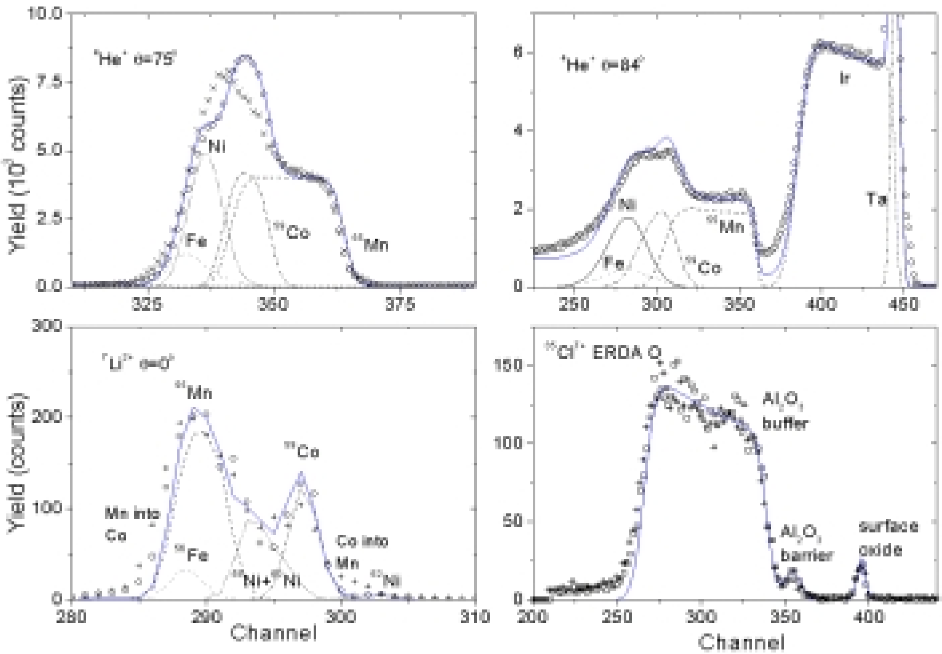

Fig. .1RBS, heavy ion RBS and ERDA data for a spin valve structure as deposited (circles) and annealed (crosses).

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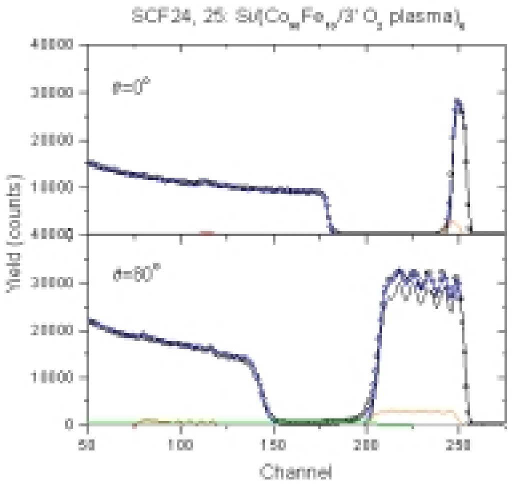

Fig. 2. RBS spectra taken at normal incidence and at a 80º grazing angle of incidence of a Si/ $(Co_{90}Fe_{10}$ / 3' O_2 plasma$)_6$ sample.

magnetic signal on annealing, in which the magnetic moment of the CoFe layer decreases by a factor of two due to inclusion of Mn. This is accompanied by a reduction and even disappearance of the TMR signal. Inclusion of diffusion barriers has lead to making the tunnel junctions with best thermal stability, as well as highest TMR signal, so far reported [1,2].

Spin valves with typical structure Si/Ta 70Å/NiFe 50Å/MnIr 90Å/CoFe 14Å/oxidation/CoFe 25Å/Cu 20Å/CoFe 26Å/oxidation /Ta 20Å, for use as read elements in read/write magnetic heads, were also analysed [3]. The RBS data shown in Figure 1, for a specially prepared multilayer sample, showed that a 15±1 Å CoFe oxide layer grows at the surface of the CoFe layers. This leads to a 13.6% magnetoresistance effect, as compared with 6% in similar spin valves without the oxide layer.

Further work

This work reflects a long standing collaboration between ITN and INESC. It shall continue in the future, as the fast change in the structure of advanced magnetic materials means powerful characterisation methods will continue to be required.

Published (or in press) work

[1] Cardoso, S., Freitas, P.P., de Jesus, C., Soares, J.C., High thermal stability tunnel junctions, *J. Appl. Phys.* **87** (2000) 6058.

[2] Cardoso, S., Ferreira, R., Freitas, P.P., Wei, P., Soares, J.C., Influence of Ta antidiffusion barriers on the thermal stability of tunnel junctions, *Appl. Phys. Lett.* **76** (2000) 3792.

[3] Freitas, P.P., Wei, P., Barradas, N.P., Soares, J.C., Almeida, B., Sousa, J.B., Magnetoresistance enhancement in specular, bottom-pinned, $Mn_{83}Ir_{17}$ spin valves with nano-oxide layers, *Appl. Phys. Lett.* **77** (2000) 1020.

[4] Kling, A., da Silva, M.F., Soares, J.C., Freitas, P.P., Baptista, D.L., Zawislak, F.C., Investigation of an 18Å Al_2O_3 layer in a magnetic multilayer system by Rutherford and resonant scattering, *Nucl. Instrum. Methods **B*** **161** (2000) 549.

[5] Wei, P., Cardoso, S., de Jesus, C.M., Soares, J.C., Freitas, P.P., da Silva, M.F., RBS study of the interdiffusion effect between CoFe/MnIr layers in tunnel junctions, *Nucl. Instrum. Methods **B*****170** (2000) 205.

[6] Barradas, N.P., Wei, P., da Silva, M.F., Soares, J.C., Kreissig, U., Arnoldbik, W., Cardoso, S., Freitas, P.P., High resolution IBA analysis of complex ultra-thin magnetic systems: potential and limitations; *IAEA TECDOC*, Vienna, in press.

Thin Films

E. Alves, N.P. Barradas, N. Franco, A.D. Sequeira, M.F. da Silva, J.C. Soares, L. Rebouta[a], C.J. Tavares[a], C. Jeynes[b], R. Silva[b], U. Kreissig[c], T. Telbizova[c]

Objectives

Thin films are present in the vast majority of modern advanced materials. As such, different activities with that common denominator are carried out using the **Ion Beam Laboratory** facilities at ITN. The objective is to study, and develop, particular systems of interest. These are by nature collaborative works that involve other laboratories.

Results

The main areas of research within thin films were this year:

- **Structure determination of (Ti,Al)N/Mo multilayers** [1-3]. These are being developed for wear prevention in steel tools and cutting applications. The multilayers were analysed with RBS and XRD. Their composition and interfacial roughness were determined.
- **Accurate depth profiling of complex optical coatings** [4]. These are an enabling component of many optical devices. The systems are extremely complex, with tens of very thin multi-elemental layers leading to demanding analysis problems. It was shown that RBS allied to novel algorithms for inverse problem solving were very successful in determining the structure of the filters with high precision.
- **Composition of NiTaC films** [5]. These are used in systems that combine exceptional hardness and excellent corrosion performance for tribological surface coatings. Their exact stoichiometry determines their properties. The C content is very difficult to measure quantitatively. It was shown that precise measurements could be obtained by using proton elastic backscattering experiments and careful data analysis procedures.
- **Growth and characterisation of amorphous carbon films doped with nitrogen** [6]. These are of interest to the electronics industry as possible cheap semiconductors, especially for device passivation. Nitrogenation is a possible method for the doping of the films, but current processes also lead to the inclusion of hydrogen. The content of N and H of the films was measured and related to observed changes in their bandgap.
- **Simultaneous and consistent analysis of RBS, ERDA and NRA data from thin films** [7]. Complex thin films often require a combination of techniques to derive the needed information. This leads to problem of effective and efficient data processing. We developed a method to analyse in a fully self-consistent and automatic way data from three different, complementary, techniques.
- **Coherent amorphisation of Ge/Si multilayers with ion beams** [8]. The ballistic nature of ion implantation leads to the formation of different defect structures through the implanted layer. The knowledge of these structures and their stability is essential for technological applications. We studied defect formation and the evolution of damage with ion fluence.
- **Ion nitriding of aluminium** [9]. Al and Al-based alloys have high strength to weight ratio, corrosion resistance and formability, but due to low surface hardness and wear resistance their application is restricted. We studied nitridation of the Al surface, in particular the growth kinetics of the surface AlN layer.

Published (or in press) work

[1] Tavares, C.J., Rebouta, L., Alves, E.J., Structure Determination of (Ti,Al)N/Mo Multilayers, *Thin Solid Films* **373** (2000) 287.

[2] Vaz, F., Rebouta, L., Goudeau, P., Pacaud, J., Garem, H., Riviere, J.P., Cavaleiro, A., Alves, E., Characterization of $Ti_{1-x}Si_xN_y$ Coatings, *Surf. Coat. Technol.* **133-134** (2000) 307-313.

[3] Rebouta, L., Tavares, C., Aimo, R., Wang, Z., Pischow, K., Alves, E., Rojas, T.C., Odriozola, Hard Nanocomposite Ti-Si-N Coatings Prepared by dc Reactive Magnetron Sputtering, *Surf. Coat. Technol.* **133-134** (2000) 234-239.

[4] Jeynes, C., Barradas, N.P., Rafla-Yuan, Hichwa, B.P., Close, R., Accurate Depth Profiling of Complex Optical Coatings, *Surf. Interface Analysis* **30** (2000) 237-242.

[5] Jeynes, C., Barradas, N.P., Wilde, J.R., Greer, A.L., Composition of TaNiC Thick Films using Simulated Annealing Analysis of Elastic Backscattering Spectrometry Data, *Nucl. Instrum. Methods* ***B*161-163** (2000) 287-292.

[6] Barradas, N.P., Khan, R.U.A., Anguita, J.V., Silva, S.R.P., Kreissig, U., Grötzschel, R., Möller, W., Growth and Characterisation of Amorphous Carbon Films Doped with Nitrogen, *Nucl. Instrum. Methods* ***B*161-163** (2000) 969-974.

[7] Barradas, N.P., Parascandola, S., Sealy, R., Grötzschel, B.J., Kreissig, U., Simultaneous and Consistent Analysis of NRA, RBS, and ERDA Data with the IBA Data Furnace, *Nucl. Instrum. Methods* ***B*161-163** (2000) 308-313.

[8] Alves, E., Sequeira, A.D., Franco, N., da Silva, M.F., Soares, J.C., Sobolev, N.A., Carmo, M.C., Coherent Amorphisation of Ge/Si Multilayers with Ion Beams, accepted by *Nucl. Instrum. Methods B.*

[9] Telbizova, T., Parascandola, S., Prokert, F., Barradas, N.P., Richter, E., Möller, W., Ion Nitriding of Al: Growth Kinetics and Characterisation of the Nitride Layer; accepted by *Surface and Coatings Technology*.

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Advanced Materials for Fusion Technology

L.C. Alves, A. Paúl, E. Alves, M.R. da Silva, A. A. Melo, M.F. da Silva, J.C. Soares, L. Rebouta[a], A. La Barbera[b], B. Riccordi[b], M. A. Centeno[c], J.A. Odriozola[c], F. Scaffidi-Argentina[d], M. B. H. Breese[e]

Objectives

The development of fusion power plants requires research in advanced materials with low activation under neutron flux and good performance properties. Presently the ITN is involved in four tasks of the European Fusion Development Agreement (EFDA) Technology Workprogramme related with the materials for fusion technology field. The tasks and their objectives are the following:

- TTMA-001-7, SiC/SiCf ceramic composites.
  Study of the chemical compatibility of SiC/SiCf ceramic composites exposed to Li salts under working conditions.
- TTBB-005-9, Development of Ceramic Breeder Pebble Beds.
  Surface characterisation of Li_4SiO_4 and Li_2TiO_3 ceramic breeders and study of the chemical interactions of the ceramic breeders with purge gas and structural materials.
- TTBB- 007-10, Development of Beryllium Pebble Beds.
  Measurement of the electrical resistivity of the Beryllium Pebble Bed in air and in typical purge gas environment (He+0.1 % H).
- TTMS-006-Qualification of high performance steel.
  Development and study of RAFM/RAFM ODS alloys with improved resistance (mechanical and chemical) at higher temperatures than standard RAFM alloys.

Results

In the SiC/SiC$_f$ ceramic composites project works are related with the characterisation of corroded surfaces and impurity mapping when the material is exposed to Li_4SiO_4 or Li_2TiO_3 at 800 ºC during different intervals of time. Simultaneous PIXE and RBS spectra were collected using proton microbeams (~3 µm spatial resolution). Results of this research [1-3] show the formation of Ti rich clusters and that there are surface alterations after reaction with Li salts. As a rule, the samples exposed to Li_4SiO_4 or to Li_2TiO_3 present a strong depletion of C in the first layers which is accompanied by a Li and O diffusion that extends at least to 25 µm after only 1000 h of exposure. A distinct behaviour could be observed in some zones of the sample exposed to Li_2TiO_3 during 1000 h (figure 1). These zones present high concentration of C with relatively small thickness (1.5µm) that somehow prevents or reduces the diffusion of O and Li into the sample bulk.

The Li ceramic breeders project is related with the surface composition of Li_4SiO_4 and Li_2TiO_3 specimens after compatibility tests with SiC/SiC$_f$ composites [1-3]. Results show that C is present in the Li_4SiO_4 pebbles surface even for the virgin sample and they do not show any reaction with C

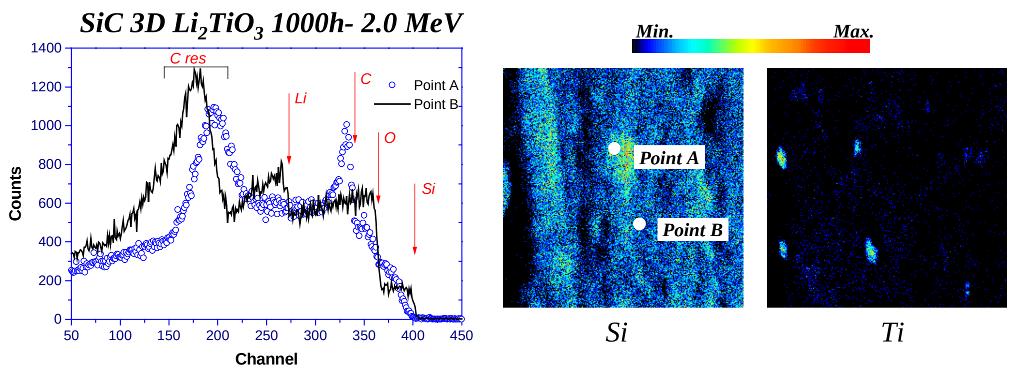

Figure 1. 500µm² scan elemental maps of Si and Ti for the SiC sample exposed during 1000h to Li_2TiO_3 showing the formation of Ti precipitates. And RBS spectra from points A and B.

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[d] Forschungszentrum Karlsruhe-IKET (Germany).
[e] University of Surrey (United Kingdom).

from the SiC/SiC$_f$. They also show the formation of a thin Si surface layer with ~100nm thickness. The material is not homogeneous as different pebbles present large differences in the Si (figure 2). The Li_2TiO_3 ceramic pebbles do not show any significant change in composition from the virgin and the annealed samples. Only at the proton resonant energy a small amount of C can be found in the surface layer that, nevertheless, can be responsible for the observed colour transition from white to brown in the virgin and annealed samples.

The Be pebble bed development project is centred in the research of the resistivity and characterisation of beryllium pebble bed in reducing He + 0.1 % H_2 atmosphere. It was observed [4] that the oxide scale present on the beryllium pebble surfaces, and the limited contact between the pebbles due to the bed porosity, led to a resistivity which is about two orders of magnitude higher than that of steel. Ion beam analysis techniques are used to investigate their impurity content and distribution as well as the surface oxidized layer. Results revealed the homogeneity of the Be pebbles and some inclusions of Ca due to some surface contamination. The main impurities in the pebbles were detected by the PIXE technique were Ti, V, Cr, Mn, Fe, Ni, and Cu. We notice also the presence of U with concentrations below 14 µg/g. Neutron activation analysis of a single Be pebble was used to confirm the presence of uranium in the pebbles and allowed to detect also the presence of traces of gold.

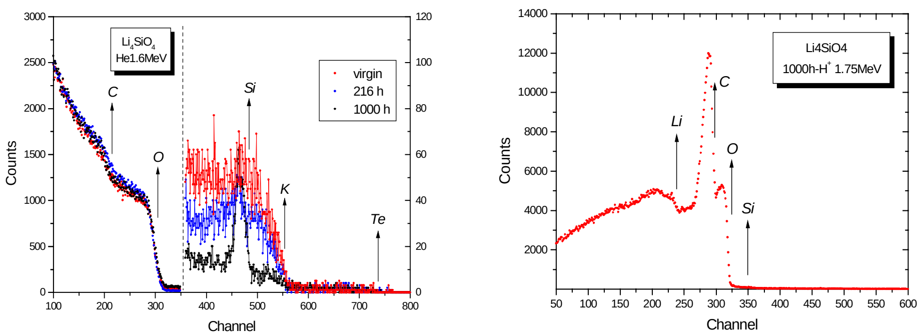

Figure 2. µRBS of Li_4SiO_4 ceramic pebbles: Left) virgin and exposed samples analysis with 1.6 MeV He^+ beam show the formation of a Si surface layer; Right) RBS C signal is enhanced through the use of a proton beam of 1.75 MeV.

The Qualification of High Performance Steel project is related with the fabrication and characterisation of reduced activation ferritic-martensitic alloys and U-doped standards. Several experimental alloys were fabricated in vacuum/gas induction furnace in 100g ingots. Alloy compositions are made starting from the F-82H composition, which will be used as reference. Variations in the composition of other elements will be pursued in order to increase the high temperature resistance. Ranges for the alloy elements are: Cr 7.7-13 wt%, Si 0.03-0.8 wt%, N 0.008-0.02 wt%, W 0.8-2 wt%, Ta 0.02-0.1 wt%, V 0.15-0.4 wt%, Ti 0.001-0.1 wt%. C will be kept constant at 0.09 wt%. Those alloys are actually being characterised in the as-cast condition. F-82H alloy has been doped with U in order to obtain standards with low U levels (µg/g). Actually the U levels obtained, as determined using PIXE, are 56 µg/g using metallic U, with an efficiency of 0.005 ($U_{measured}$/ $U_{expected}$) and 47 µg/g when Sn was added with efficiency five times higher than the previous.

Published (or in press) work

[1] Alves, L.C., Paúl, A., Alves, E., da Silva, M.F., Soares, J.C., Rebouta, L., La Barbera, A., Riccardi, B., Centeno, M.A., Odriozola, J.A., Surface Studies of SiC/SiC$_f$ Composites Exposed to Relevant Fusion Reactor Conditions, *Surf. Interface Anal.* **30** (2000) 98-100.

[2] Alves, L.C., Breese, M.B.H., Alves, E., Paúl, A., da Silva, M.R., da Silva, M.F., Soares, J.C., Micron-Scale Analysis of SiC/SiC$_f$ Composites using the new Lisbon Nuclear Microprobe, *Nucl. Instr. and Meth.* ***B*** **161-163** (2000) 334-338.

[3] Alves, L.C., Alves, E., da Silva, M.F., Soares, J.C., Paúl, A., La Barbera, A., Riccardi, B., Study of Solid State Reactions of SiC/SiC$_f$ Composites Using Microbeams, accepted for publication in *Nucl. Instr. and Meth.*

[4] Alves, E., Alves, L.C., da Silva, M.F., Melo, A.A., Soares, J.C., Scaffidi-Argentina, F., Influence of Temperature and Pressure on the Beryllium Pebble Bed Electrical Resistivity, *Fusion Technology* **38** (2000) 320-325.

Further Work

- Studies of the impurities (level and distribution) and chemical stability in fusion relevant conditions of new 3D SiC/SiC$_f$ composites.
- Chemical behaviour and compatibility of ceramic breeders with structural materials will be further investigated.
- Measures of Be pebble bed electrical resistivity under purge gas exposure and neutron irradiation.
- Characterisation of the RAFM experimental alloys and fabrication of U-doped standards starting from U intermetallics.

Synthesis of New Compounds by High Fluence Ion Implantation

A. Metastable alloys in Al- and Ti- system, Produced by Ion Implantation and Laser Processing

L.M. Prudêncio, M. Vilarigues, R.C. da Silva, A.D. Sequeira(1), M.F. da Silva, J.C. Soares,
O. Conde(2), R. Vilar(3)

Objectives

Production and study of Al-based or Ti-based surface alloys made by alloying Cr into aluminium and titanium substrates, using high fluence ion implantation, to develop wear and corrosion resistant Al and Ti based light alloys.

Investigation of the best set of implantation parameters, *viz*. target temperature, fluence and beam power density necessary to produce Al-Cr and Ti-Cr surface alloys. Knowledge of the formation, transport behaviour of Cr, stability and transformation mechanisms of these alloys as a function of temperature; identification of the microstructures formed.

Results

High purity polycrystalline Al and Ti discs were implanted with Cr fluences in the range 1-5×10^{17}/cm^2 at different substrate temperatures. Annealing programmes were put forward in order to study the stability and evolution of the so formed systems.

- *Al-Cr system*

In the Al-Cr system it was found that by ion implantation with high fluences only the $Al_{86}Cr_{14}$ and $Al_{13}Cr_2$ intermetallic compounds are formed [Prudêncio, L.M., MSc thesis, 1999, unpublished] and [1]. The conditions for the direct formation of these intermetallics were established. The stability and transformation of $Al_{86}Cr_{14}$ and $Al_{13}Cr_2$ was accessed, and the temperature domains of stability for each of these intermetallics were identified.

For temperatures below 200 ºC no intermetallic compounds of any type are detected: all Cr is retained in the Al host matrix, either dissolved or in Cr-rich aggregates, too small to be detected by GIXRD.

For temperatures ≥ 400 ºC $Al_{13}Cr_2$ is the predominant stable compound. In the range ≥ 250 ºC to < 400 ºC the predominant compound that forms is $Al_{86}Cr_{14}$, which transforms by annealing at temperatures ≥ 400 ºC in $Al_{13}Cr_2$.

Higher doses result in larger precipitates, ~ 20 nm for $Al_{86}Cr_{14}$, formed by implantation with 2×10^{17}Cr/cm^2, to ~200 nm for $Al_{13}Cr_2$, formed by implantation with 5×10^{17}Cr/cm^2.

- B. *Ti-Cr system*

In contrast with the case of Al, the results obtained so far show that no intermetallic compounds are formed, irrespective of the implantation conditions that have been used [2]. While implantations at temperatures from RT up to 800 ºC lead to peak shaped concentration profiles, with maximum Cr concentrations of up to 55 at.%, implantations at temperatures in excess of 900 ºC lead to long range diffusion of Cr. The same effect is observed also after annealing at similar temperatures. As conventional MeV RBS spectrometry is unable to handle such long range diffusion, a proton microbeam was used to extract concentration profiles for Cr, by examinig cross-sections of the samples cut along the implantation direction. The technique successfully allowed to obtain the complete Cr profiles, and thus to show that Cr diffuses as far as 100 µm, while at 1000 ºC for one hour.

An isothermal annealing programme at 600 ºC for periods from 1 to 24 hours revealed transport of Cr from the near surface region to a deep sink, near the end-of-range of the implantation profile, leading to a double humped distribution, that dissolves by further annealing or at higher temperatures.

Published (or in press) work

[1] Prudêncio, L.M., da Silva, R.C., da Silva, M.F., Soares, J.C., Conde, O., Vilar, R., Modification and characterisation of Al surfaces implanted with Cr ions, *Surface and Coatings Technology* **128-129** (1-3) (2000) 166-169.

[2] Metastable alloys in ti-cr system produced by ion implantation and laser processing, Contract no. PRAXIS/P/CTM/10037/98, 1st Progress Report to the FCT, 2000.

Further work

- *Al-Cr system*

Although the research contract is closed, TEM work is planned to precisely access the morphology and size distribution of the precipitates, as well as corrosion work to access the suface chemistry.

- *Ti-Cr system*

Modelling of Cr transport.

TEM work to access the morphology and microstructure of the system, as well as corrosion work to access the suface chemistry.

Laser alloying Cr with Ti, followed by characterisation work as performed for ion implanted samples, in order to prepare hard and corrosion resistant surface layers.

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B. Channeled Ion Beam Synthesis of $HfSi_2$

A.R. Ramos, J.G. Marques [a], M.R. da Silva [b], O. Conde [c], M.F. da Silva, J.C. Soares

Objectives

Hafnium disilicide ($HfSi_2$) has one of the lowest resistivities and highest melting point among refractory silicides. It has been formed by sputtering and by electron-gun evaporation of Hf thin films on silicon wafers with heat treatments in the 700-1100ºC range. Ion implantation has been shown to promote the formation of $HfSi_2$ at lower temperatures but continuous stoichiometric layers could not be prepared due to the high sputtering yield of Hf. We proposed to overcome these difficulties by channeled ion implantation.

Results

A stoichiometric polycrystalline $HfSi_2$ surface layer, 1660 Å thick, was formed by channeled implantation of Hf^{2+} to a fluence of 2.3×10^{17} at/cm^2 at 600ºC. A multi-sep annealing procedure -800/900/1000ºC- was found to favour layer stability compared to a two-step annealing -700/1000ºC- (see Fig. 2). Minimum resistivity values of 60 μΩcm were obtained after the 1000ºC annealings (see Fig.1a). In lower fluence implanted samples (1.5×10^{17} Hf/cm^2), the two annealing procedures resulted in similar Hf diffused profiles. In the multi-step procedure, evidence of channeling in the Hf profile was seen immediately after the 800ºC step and the minimum yield reached its lowest value of 0.76 after the 900ºC step. This corresponds to a much lower temperature than reported earlier (1100ºC) for the onset of epitaxy [4]. The width and height of the random Hf profile remained unchanged until the 1000ºC step, where Hf diffusion began. In this case, resistivity increases after the 1000ºC annealing, resulting from layer degradation (see Fig. 1b) [5,6].

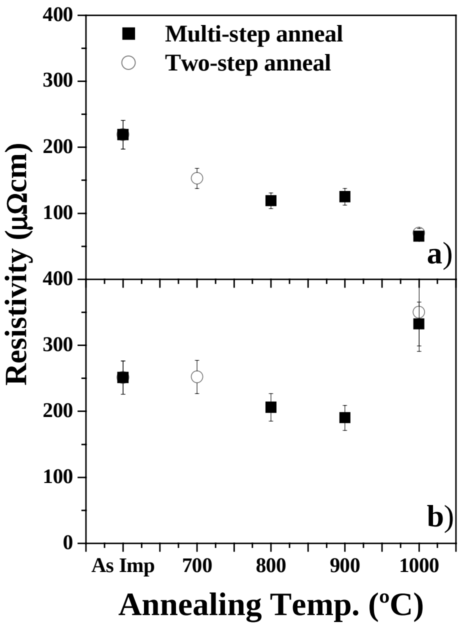

Fig. 1 Glancing incidence RBS spectra (θ=80) of the 2.3×10^{17} Hf/cm^2 implanted sample after both annealing procedures: multi-sep annealing (800/900/1000ºC) and two-step annealing (700/1000ºC).

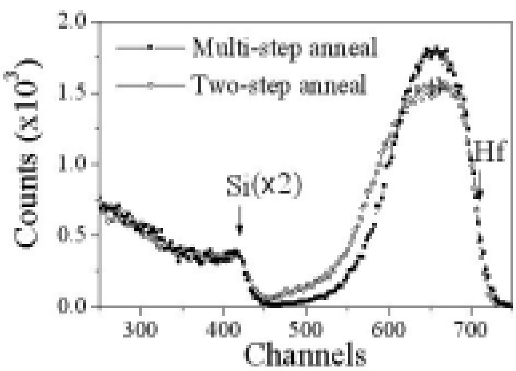

Fig. 2 Variation of resistivity with annealing temperature for samples implanted with 2 different fluences: a) 2.3×10^{17} Hf/cm^2 and b) 1.5×10^{17} Hf/cm^2. The squares and open circles refer to two annealing procedures: multi-sep annealing (800/900/1000ºC) -^{v}T- and two-step annealing (700/1000ºC) - -.

Published (or in press) work

[4] Chang, C.S., Nieh, C.W., Chen, L.J., *J. Appl. Phys.* **61** (1987) 2393.

[5] Ramos, A.R. *et al.*,, Channeled Ion Beam Synthesis of $HfSi_2$, *Nucl. Instr. and Methods,* ***B*161-163** (2000) 909-912.

[6] Ramos, A.R., Preparação de Silicetos Metálicos para Aplicação em Microelectrónica, PhD Thesis, Lisbon University, Lisbon, Portugal, 2000.

Further work

Assessment of the influence of the native O content in the silicon waffers in $HfSi_2$ formation.

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[b] Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
[c] FCUL- Faculdade de Ciências da Universidade de Lisboa, Dep. Física, Ed C4, P-1749-016, Lisboa, Portugal.

C. Ion Beam Synthesis of Chromium and Cobalt Silicide on Porous Silicon

A.R. Ramos, O. Conde[a], F. Pászti[b], E. Kotai[b],G. Battistig[c], É. Vázsonyi[c], M.R. da Silva[a], M.F. da Silva, J.C. Soares

Objectives

Preparation of reliable, low resistivity contacts on porous Si devices, by inserting a silicide layer in between the metal contact and silicon by ion implantation. Porous silicon (PS) is extensively investigated for its electro-luminescence property. Its use could allow the integration of optical and electronic units into a single device with conventional technology. Formation of electric contacts on PS is a basic requirement. By implanting ions routinely used in silicide formation, *e.g.* 100-200 keV Cr and Co ions, preparation of compact silicide contacts on PS might be achieved in one single step.

Results

- *Cr implantation*

Different types of porous Si layers several µm thick were implanted with 170 keV Cr+ ions to fluences of 3x1017 ions/cm2 both at RT and 450°C and then annealed (700°C 90min + 1000°C 15min). The porous to compact transition was investigated by the O resonance method . The formed silicide compounds were studied by RBS, glancing incidence XRD and four point probe resistivity measurements. According to resonant RBS (O, C) and ERD (H) measurements the light impurities were partially expelled from the forming silicide layer. The resistivity, in spite of the remaining high impurity level, is surprisingly low. The formed silicide type is related to the original impurity level as well as to implantation temperature and annealing (Fig.3) [7].

- *Co implantation*

Under the experimental conditions used, in PS with an O/Si ratio <0.30 it is possible to form a good quality cobalt disilicide layer immediately after implantation. The light impurities present in the original substrate partly escape from the implanted layer, pilling up behind it. In more contaminated substrates, another more Co rich phase appears (CoSi). Above 0.70 O/Si ratio no silicide can be detected by x-ray diffraction (fig. 4b). Best electrical properties are obtained with LT implanted samples, though their resistivity is still ~3 times higher than their monocrystalline counterpart (15 *vs.* 45 µΩcm) (Fig. 4a) [8].

Further work

TEM work to access the morphology.

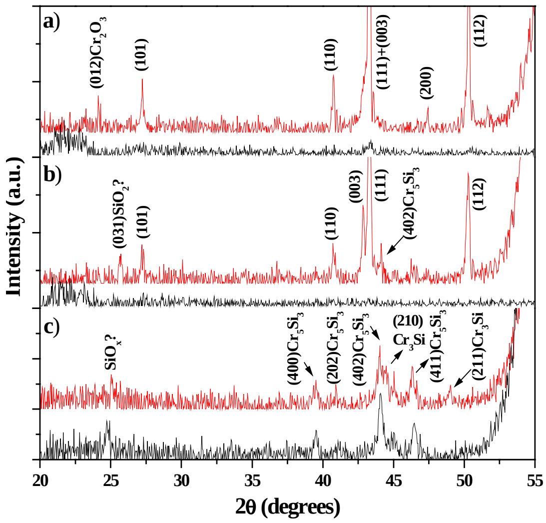

Fig. 3 X-ray diffraction results for a) C6HT, b) C6OXHT and c) SOXHT samples (Cr implanted samples with increasing O/Si ratio in the porous layer). Lower and upper spectra correspond to as implanted and annealed (700°C, 90 min) samples, respectively. The peaks indicated simply by their lattice plane correspond to $CrSi_2$.

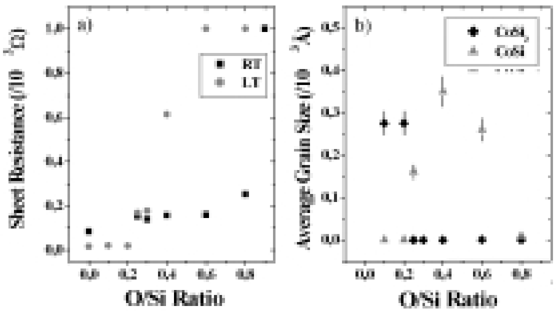

Fig. 4 (a) Sheet resistance values for samples implanted at 350ºC (LT) and at room temperature (RT). (b) Average grain size for LT samples vs. O/Si ratio in the buried porous layer.

Published (or in press) work

[7] Ramos, A.R., *et al.*, Ion Beam Synthesis of Chromium Silicide on Porous Silicon, *Nucl. Instr. and Methods* ***B*161-163** (2000) 926-930.

[8] Ramos, A.R., *et al.*, Synthesis of Cobalt Silicide on Porous Silicon by High Dose Ion Implantation, accepted to *Nucl. Instr. And Methods*, **B**

[a]FCUL- Faculdade de Ciências da Universidade de Lisboa, Dep. Física, Ed C4, P-1749-016, Lisboa, Portugal.
[b] KFKI-Res. Inst. for Particle and Nuclear Physics, PO BOX 49 H-1525, Budapest, Hungary.
[c]MTA-Res. Inst. for Technical Phys. and Materials Science, PO BOX 49 H-1525, Budapest, Hungary.microstructure of the system.
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e^--γ Perturbed Angular Correlations and Emission Channeling at ISOLDE/CERN

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Objectives

The Nuclear Solid State Physics group works at ISOLDE since 13 years with the e^--γ Perturbed Angular Correlations and Emission Channeling Techniques, which are complementary tools to the ion beam techniques in Sacavém. Our work is currently centered in three research subjects approved by the ISOLDE and Neutron-Time-of-Flight Scientific Committee: a) Studies of High–Tc Superconductors Doped with Radioactive Isotopes; b) Studies of Colossal Magnetoresistance Oxides with Radioactive Isotopes; c) Lattice Site Location of Transition Metals in Semiconductors.

Results

a) Studies of High –Tc Superconductors Doped with Radioactive Isotopes (IS360)

In the $Hg_1Ba_2R_{(n-1)}Cu_nO_{(2n+2+\delta)}$ (T_C >130 K) high-Tc superconductor family the aim is to characterize at the atomic scale the non-stoichiometric doping oxygen (O_δ) that goes to the Hg planes, regulating the injection of charge carriers at the superconducting CuO_2 planes, and to follow structural / electronic perturbations which are observable, particularly, in the Hg neighborhood. We have shown that the PAC technique is highly sensitive to the presence and concentration of O_δ and have proved that electronic / structural perturbations are occurring in the O(2)-HgO(2) apical chain neighborhood at low temperature [1, 2, 3, 4].

We have studied the atomic behavior and lattice site of Hg/Au implanted $YBa_2Cu_3O_{6+x}$ (YBCO), since both Hg and Au are reported to improve the lattice stability increasing Tc. We have shown that Hg goes to the Cu(1) site in the YBCO lattice [5]. We intend to further study the lattice site localization of Ca and Ag, since both elements contribute to decrease band-bending effects in grain interfaces, thus improving critical current values [4].

b) Studies of Colossal Magnetoresistive Oxides with Radioactive Isotopes (INTC/P132)

We are studying Colossal Magnetoresistive (CMR) oxides with the aim to provide local and element selective information on some of the doping mechanisms that rule electronic interactions and magneto-resistance, in a complementary way to the use of conventional characterization techniques [6]. Preliminary PAC results obtained for ^{111m}Cd implanted $La_{1-x}Cd_x\,MnO_3$ pellets and thin films, show very different (and unexpected) macroscopic magneto-electric properties from $La_{1-x}Ca_x\,MnO_3$. There the presence of a magnetic filed of about 3T at the Cd place is revealed below the Curie temperature, around 180K. This is already a surprising result since strong magnetic fields are only expected to be located at the Mn sites [7].

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c) Lattice Site Location of Transition Metals in Semiconductors (IS368)

The main goal is to determine the lattice site location and dopant–defect interactions of Er, Yb, Fe, Cu and As implanted Si, GaN [8] and diamond by EC and PAC experiments. At ITN the RBS/Channeling technique is used to study the samples' crystalline quality and the recovery of implantation defects.

Cu represents a widespread contaminant in Si processing and is responsible for several deep levels which act as recombination centers for electrons and holes and degrade the performance of devices. β^- EC lattice location experiments using the radioactive isotope ^{67}Cu ($t_{1/2}$=61.9 h) implanted into single-crystalline Si show that the majority of implanted Cu occupies near-substitutional sites. As most-likely lattice location we suggest a displacement of 0.51(7) Å along <111> directions from substitutional sites to bond center positions. The annealing behavior shows that more than 90% of Cu recovers to fully substitutional sites, being remarkably stable, with an estimated dissociation energy of 2.2 eV [9, 10]. Fe acts as a deep acceptor if incorporated on substitutional III sites in the cubic III-V semiconductors such as GaAs, GaP or InP. The most prominent example with respect to applications is InP, where doping with Fe is used to produce semi-isolating material. Much less is known about Fe in the hexagonal III-V semiconductor GaN. The lattice location of implanted Fe was studied by EC in the decay of ^{59}Fe after room temperature implantation of ^{59}Mn at a dose of 1.0×10^{12} cm^{-2} and annealing up to 900^{o}C. We have given direct evidence that Fe is mainly incorporated on substitutional Ga sites. Annealing the implanted sample up to 900°C did not noticeably affect the substitutional Fe fraction [11].

Published (or in press) work

[1] Correia, J.G., Araújo, J.P., Marques, J.G., Ramos, A.R., Melo, A.A., Soares, J.C., and the ISOLDE Collaboration, Electron-Gamma PAC: New Possibilities for NQI Studies, *Zeitschrift für Naturforschung* **55a** (2000) 3.

[2] Correia, J.G., Araújo, J.P., Loureiro, S.M., Toulemonde, P., Le Floch, S., Bordet, P., Capponi, J.J., Gatt' W.Tröger, R., Ctortecka, B., Butz, T., Haas, H., Marques, J.G., Soares, J.C. , Local Oxygen Probing in the $HgBa_2CuO_{4+\delta}$ high-T_C Superconductor, *Physical Review **B*** **61** (2000) 11 769 - 11 775.

[3] Correia, J.G., Araújo, J.P., Loureiro, S.M., Toulemonde, P., Le Floch, S., Bordet, P., Capponi, J.J., Gatt, R., Tröger, W., Ctortecka, B., Butz, T., Haas, H., Marques, J.G., Soares, J.C., Local Probing of Hg Neighborhood in Oxygen and Point Defects Probing in $HgBa_2CuO_{4+\delta}$, *Physica **C*** **341** (2000) 1969-1972.

[4] Correia, J.G., Araújo, J.P., *et. al*, Studies of High-Tc Superconductors Doped with Radioactive Isotopes, CERN/ISC 96-30, ISC P86, IS360, addendum to IS360 approved by the INTC/CERN scientific committee 2000.

[5] Correia, J.G., Araújo, J.P., Marques, J.G., Ramos, A.R., Lourenço, A.A., Amaral, V., Galindo, V., Senateur, J.P., Weiss, F., Wahl, U., Melo, A.A., Soares, J.C., Sousa, J.B., and the ISOLDE Collaboration, Electron-Gamma Perturbed Angular Correlation Studies on High-T_C Superconductors", *Hyperfine Interactions* **129** (2000) 461-473.

[6] Amaral, V.S., Araújo, V., Correia, J.G., *et. al*. Studies of Colossal Magnetoresistive Oxides with Radioactive Isotopes, INTC P132, proposal approved by the INTC/CERN scientific committee 2000.

[7] Araújo, J.P., Correia, J.G., Amaral, V.S., Tavares, P.B., Lencart-Silva, F., Lourenço, A.A.C.S., Sousa, J.B., Vieira, J.M., Soares, J.C., and the ISOLDE Collaboration, Hyperfine Fields at the Cd Site in $La_{0.67}Cd_{0.25}MnO_3$ CMR Manganites, accepted by Hyperfine Interactions.

[8] Wahl, U., Vantomme, A., Langouche, G., Araújo, J.P., Peralta, L., Correia, J.G., and the ISOLDE collaboration, Emission Channeling Studies of Pr in GaN, *Journal of Applied Physics* **88** (2000) 1319-1324.

[9] Wahl, U., Vantomme, A., Langouche, G., Correia, J.G., and the ISOLDE collaboration, Lattice Location of ion Implanted Cu in Si, *Physical Revue Letters* **84** (2000) 1495-1498.

[10] Wahl, U., Vantomme, A., Langouche, G., Araújo, J.P., Peralta, L., Correia, J.G., and the ISOLDE collaboration, Lattice location of implanted Cu in highly-doped Si, *Applied Physics Letters*, in press.

[11] Wahl, V., Vantomme, A., Langouche, G., Peralta, L., Correia, J.G., and ISOLDE Collaboration, Direct Evidence for Implanted Fe on Substitutional Ga Sites in GaN, *Appl. Phys. Lett.*, in press.